

## **SURFACE AREA, AND OXIDATION EFFECTS ON NITRIDATION KINETICS OF SILICON POWDER COMPACTS**

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### **ABSTRACT**

Commercially available silicon powders were wet-attrition-milled from 2 to 48 hr to achieve surface areas (SA's) ranging from 1.3 to 70 m<sup>2</sup>/g. The surface area effects on the nitridation kinetics of silicon powder compacts were determined at 1250 or 1350°C for 4 hr. In addition, the influence of nitridation environment, and preoxidation on nitridation kinetics of a silicon powder of high surface area (≈63 m<sup>2</sup>/g) was investigated. As the surface area increased, so did the percentage nitridation after 4 hr in N<sub>2</sub> at 1250 or 1350°C. Silicon powders of high surface area (>40 m<sup>2</sup>/g) can be nitrided to > 70% at 1250°C in 4 hr. The nitridation kinetics of the high-surface-area powder compacts were significantly delayed by preoxidation treatment. Conversely, the nitridation environment had no significant influence on the nitridation kinetics of the same powder. Impurities present in the starting powder, and those accumulated during attrition milling, appeared to react with the silica layer on the surface of silicon particles to form a molten silicate layer, which provided a path for rapid diffusion of nitrogen and enhanced the nitridation kinetics of high surface area silicon powder.

[KEY WORDS: Nitridation kinetics; High-surface-area silicon; Impurity and oxidation effects]

### **INTRODUCTION**

Monolithic reaction-bonded silicon nitride (RBSN) material is typically fabricated by first consolidating 3 to 50-μm-sized silicon powders into the desired shape and then nitriding the object in N<sub>2</sub>(g) or in a N<sub>2</sub>-H<sub>2</sub>(g) environment for 50 to 100 hr between 1350 and 1450°C [1]. This processing methodology, however, cannot be used for the fabrication of RBSN composites using small diameter ceramic fibers because of fiber degradation at high processing temperatures[2]. Also, it is difficult to achieve high-volume-fraction composites using silicon

powders ranging in diameter from 3 to 50  $\mu\text{m}$ . Therefore for the development of RBSN composites, there is a need to develop a shorter time, and lower temperature nitridation cycle using sub-micron silicon powders.

Low temperature nitridation cycles have been developed by using laser synthesized high purity nano-sized silicon powders[3], or by adding transition metal additives to commercial purity silicon powders [4-5]. Both techniques cannot be adapted to composite fabrication for the following reasons. Haggerty et al [3] reported that laser synthesized silicon powders tend to agglomerate easily, and are prone to oxidation during air exposure or in contact with many of the polymer binders typically used in RBSN processing. They have also shown that oxidation delayed, or even completely stopped the nitridation reaction depending on the degree of oxidation. On the other hand, the transition metal nitride enhancing additives are known to react with SiC fibers, or with interface coatings such as boron nitride (BN) and SiC during RBSN processing causing fiber degradation [6].

The current study had two objectives. From a basic understanding point of view, the first objective was to determine the effects of powder lots, surface area, preoxidation, and nitridation environment on nitridation kinetics. From a practical point of view, the second objective was to develop a low temperature nitridation cycle without using nano-sized silicon or transition metal nitridation enhancing additives for future RBSN composite development with small diameter SiC fibers.

## EXPERIMENTAL PROCEDURE

Three lots of silicon powders were used. The powder lots were supplied by Union Carbide (Union Carbide, Linde Division, Tonawanda, NY), Kemanord-Sicomill grade-IV (Kemanord, Ljungaverk, Sweden), and Albemarle (Albemarle Corporation, Baton Rouge, LA). For brevity, these powders are henceforth referred to as Type-A, Type-B, and Type-C, respectively. All the as-received silicon powders were attrition-milled to reduce their particle size and, hence, to increase their surface area. A  $\text{Si}_3\text{N}_4$  grinding medium was used for milling at room temperature for 2, 8, 32, and 48 hr, with Stoddard (kerosene-based fluid) as the grinding fluid. The weight ratio of silicon powder to grinding media was  $\approx 40$ . The attrition milling was accomplished by the procedure detailed in reference 7. Afterwards, the excess grinding fluid was siphoned off from the grinding vessel. Then, the silicon slurry was poured into a rectangular pan and dried for 24 hr in a vacuum oven set at  $600^\circ\text{C}$ . The dried powder was transferred to a glass jar and stored in a glove box that was purged continuously with high purity nitrogen.

The impurities in, and the particle size range and specific surface area of the silicon powders were determined respectively, by wet chemistry, laser light

scattering (Microtrac, Model 7991), and the three point Brunauer-Emmett-Teller (BET) adsorption (Micromeritics, Model ASAP 2010) techniques.

Silicon compacts, 12.7 mm in diameter and 2 to 3 mm thick, were prepared by uniaxially pressing attrition-milled silicon powder in a stainless steel die at 70 MPa. The compacts were  $\approx 45\%$  dense compared to the theoretical density of silicon (2.33 g/cc).

The silicon compacts were nitrided for 4 hr at 1250 or 1350°C in a thermogravimetric analysis unit (Model 429/409, Netzsch, Germany) equipped with a tungsten-element furnace. The nitriding atmospheres were flowing  $N_2$ (99.999%), or  $N_2+4\%H_2$  (99.99%), or  $N_2+5\%NH_3$ (99.99%). These gases were percolated through several cartridges of gettering agents to reduce oxygen and water vapor content to less than 10 ppm. After gettering, these gases typically contained 3 to 4 ppm of water vapor and oxygen.

Following nitridation, the compacts were analyzed for impurities and phase composition by wet chemistry and X-ray diffraction (XRD), respectively. The XRD runs were made at a scanning speed of 1 deg/min using standard powder diffraction equipment with a Ni filter and Cu  $K_\alpha$  radiation.

## RESULTS AND DISCUSSION

SEM examination indicates that Type A and B powders are flaky and faceted, and Type C powder is spherical. The particle size, surface area, and impurity analysis for the as-received powders are shown in Table I. According to this table, the as-received Type-A silicon powder contained significant amounts of Fe, Ni, Al, Cr, and oxygen impurities; whereas Type-B and Type-C silicon powders are relatively pure. All powders were attrition milled and then characterized similar to the as-received powders. The effect of attrition milling on particle size, surface area, and chemistry of Type-B silicon powder is shown in Table II as an example. In general, as the attrition-milling time increased, the average particle size decreased and the surface area increased, as expected, but the amount of Y, Al, and oxygen impurities also increased. The amount of Y and Al impurities varied with the attrition-milling time and reached values of  $\approx 700$  and 200 ppm, respectively, for the 48-hr-attrition-milled Type-B powder. The source of these impurities was traced to the  $Si_3N_4$  grinding medium which contained 6 wt%  $Y_2O_3$  and 2 wt%  $Al_2O_3$  as sintering additives.

### Effect of surface area on nitridation kinetics

The nitridation kinetics were determined for the compacts prepared from the as-received silicon powder lots and the powder attrition-milled for 2, 8, 32, and 48 hr. The surface area of these powders, ranged from 1.3 to 70 m<sup>2</sup>/g depending on the

Table I. Particle size, surface area, and impurity analysis of the as-received silicon powders.

	Type A	Type B	Type C
Average particle size ( $d_{50}$ ), $\mu\text{m}$	8.9	23.12	0.88
Specific surface area, m <sup>2</sup> /g	4.9	1.3	8.17
Impurities, wt%			
Carbon	0.03	0.01	0.16
Oxygen	0.42	0.7	0.48
Iron	0.5	0.02	0.01
Impurities, ppm			
Nickel	460	0.006	6
Aluminum	1000	0.002	2
Chromium	730	0.02	20
Yttrium	100	0.002	2

Table II. Particle size, surface area, and impurity analysis of attrition-milled Type-B silicon powder.

Milling time, hr	Average particle size, $\mu\text{m}$	Specific surface area, m <sup>2</sup> /g	Oxygen, wt%	Yttrium, wt%	Aluminum, ppm
2	15.94	3.6	1.01	0.002 ppm	30
8	1.44	9.6	1.45	0.002 ppm	40
32	0.54	30	3.71	0.06	120
48	0.48	63	8.87	0.17	200

attrition milling time. Fig. 1 shows typical nitridation behavior of the as-received Type-B powder and the same powder attrition-milled for 8 or 48 hr, and then nitrided in  $N_2$  at  $1250^\circ C$  for 4 hr. As the nitridation reaction progressed, the weight increased because large amounts of silicon were converted to  $Si_3N_4$ , but small amounts of silicon also evaporated as  $SiO(g)$  or  $Si(g)$ , which resulted in weight loss. In the percentage nitridation plots shown in Fig. 1, the evaporation of these gaseous

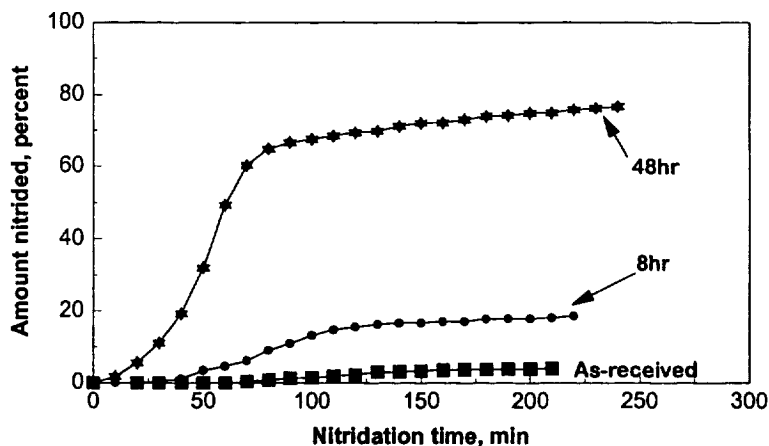


Fig. 1. Nitridation behavior of the as-received ( $SA \approx 1.3 \text{ m}^2/\text{g}$ ), and 8 hr ( $SA \approx 1.3 \text{ m}^2/\text{g}$ ) and 48 hr ( $SA \approx 1.3 \text{ m}^2/\text{g}$ ) attrition milled silicon powders in  $N_2$  at  $1250^\circ C$ .

species during the nitridation reaction was not taken into account. It is clear from this figure that there are three nitridation regions: an induction period, a rapid nitriding period, and a nitridation saturation period. As the grinding time is increased - in other words, as the surface area of the silicon powder is increased - the slope of the second region and the percent silicon nitrided in 4 hr are increased. Also noticed in Fig. 1 is that the nitridation curves for the as-received and 8-hr-attrition-milled silicon powder compacts appear to reach a plateau after 120 to 150 min, but that for the 48-hr-attrition-milled silicon powder shows increased nitridation with time. If this trend continues, it appears that complete conversion of silicon to  $Si_3N_4$  can be achieved in  $\approx 8$  hr.

Fig. 2 shows how percent nitridation varies with surface area for the three lots of attrition milled silicon compacts nitrided at  $1250$  or at  $1350^\circ C$  for 4 hr. Three main conclusions can be drawn from this figure: (1) as the surface area of the powder increases, the percentage of silicon converted to  $Si_3N_4$  also increases; (2), at the higher nitridation temperature, the conversion rate is higher, especially for the

Type-A silicon powder; (3) both the as-received and attrition milled Type-A silicon powders convert to silicon nitride to a greater extent at both nitridation temperatures than the other two lots of silicon powders. Extrapolation of the 1250°C nitridation curve with surface area suggests that the attrition-milled Type-B silicon powder with surface area  $>80 \text{ m}^2/\text{gm}$  can be completely nitrided in 4hr.

The phase and oxygen analysis of the nitrided as-received and attrition-milled Type-B powder compacts are summarized in Tables III and IV; Nitridation of these compacts were performed at 1250°C and 1350°C in  $\text{N}_2$  for 4hr. These tables demonstrate that as the surface area increases, the amounts of  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$  in the compacts increases continuously except in the case of the  $63 \text{ m}^2/\text{g}$  silicon powder compact nitrided at 1350°C, but the ratio of  $\alpha\text{-}/\beta\text{-Si}_3\text{N}_4$  (henceforth referred to as  $\alpha/\beta$  ratio) decreases. At a given nitridation temperature, the ratio of oxygen after nitridation to that before nitridation (referred to in the tables as oxygen ratio) remains nearly the same with increasing surface area, but decreases with increasing temperature of nitridation. The compacts prepared from the highest surface area ( $\approx 63 \text{ m}^2/\text{g}$ ) silicon powder and nitrided at 1350°C for 4 hr contained an oxynitride phase, and lower amounts of  $\alpha\text{-Si}_3\text{N}_4$  than the compacts prepared from most of the lower surface area powders nitrided under similar conditions. Tables III and IV also show that the total weight gain after the 4 hr nitridation at each temperature also

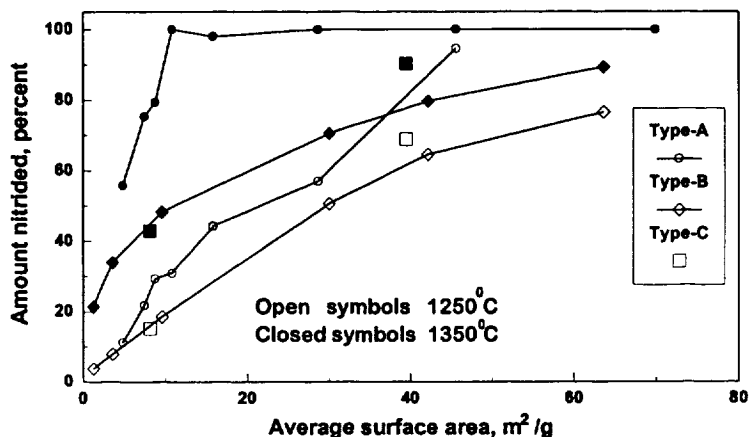


Fig. 2. Effect of surface area on amount of silicon in % converted to  $\text{Si}_3\text{N}_4$  for the as-received and attrition milled Types A, B, and C silicon powder compacts nitrided at 1250°C and 1350°C in  $\text{N}_2$  for 4hr.

Table III. Surface area effects on phase composition and oxygen ratio of Type-B silicon compacts nitrided in  $N_2$  at 1250°C for 4 hr.

Surface area, $m^2/g$	$\alpha$ - $Si_3N_4$ , wt%	$\beta$ - $Si_3N_4$ , wt%	$\alpha/\beta$ ratio	Un-reacted silicon, wt%	Oxygen ratio@	Wt. gain, %
1.3	3.7	0	-	96.3	0.71	0.80
3.6	6.7	1	6.7	92.2	0.63	3.60
9.6	12.3	6.2	2.1	81.5	0.79	10.04
30	26.3	24.3	1.2	49.4	0.76	23.08
63	40.1	36.6	1.09	23.4	0.72	32.12

@ Ratio of oxygen after nitridation to oxygen before nitridation.

Table IV. Surface area effects on phase composition and oxygen ratio of Type-B silicon compacts nitrided in  $N_2$  at 1350°C for 4 hr.

Surface area, $m^2/g$	$\alpha$ - $Si_3N_4$ , wt%	$\beta$ - $Si_3N_4$ , wt%	$\alpha/\beta$ ratio	Un-reacted silicon, wt%	$Si_2N_2O$ , wt%	Oxygen ratio@	Wt. gain, %
1.3	18.6	2.8	6.64	78.6	0	0.6	6.80
3.6	26.8	7.1	3.77	66.1	0	0.59	13.70
9.6	34.2	14	2.44	51.7	0	0.67	26.48
30	34	36.5	0.93	29.5	0	0.68	34.20
63	9.1	73.5	0.12	10.7	6.8	0.67	36.10

@ Ratio of oxygen after nitridation to oxygen before nitridation

increased with increasing surface area. However, the maximum weight gain seen in the compacts nitrided to 80% or greater conversion is  $\approx 36$  wt%, which is much lower than the theoretical value of 66 wt%. The discrepancy in the weight gain is partially due to the loss of silicon as  $SiO$  (g) and  $Si$  (g) and partially due to the

greater amounts of amorphous silica present in the finer powder, which did not nitride completely.

Increased amount of nitridation with surface area can be understood with current nitridation models[1]. It is generally accepted in RBSN literature that for initiation of the nitridation reaction, the silica layer on the surface of silicon must be disturbed. Sustaining the nitridation reaction depends on the rate of formation and growth of  $\text{Si}_3\text{N}_4$  nuclei. Devitrification or formation of a low melting glassy phase can disrupt the silica layer. Impurities such as Na, Ca, Al, Fe, Cr, Ni and Y in the silicon powder are known to react with the silica layer to form a low melting glassy phase which promote rapid diffusion of nitrogen to the silicon substrate. Of these impurities, alkaline earth and transition metal impurities are known to be effective silicate formers [4,5]. On the other hand, for continuation of the nitridation reaction, surface area of the silicon particle is important because it controls rate of formation and growth of  $\text{Si}_3\text{N}_4$  nuclei. Data shown in Tables I and II indicate that as-received Type-A silicon powder contains significant amounts of transition metal impurities. And all three powder lots show increasing amounts of Al and Y impurities with grinding time. Therefore, it appears that surface area and glassy phase formation are responsible for increased amount of nitridation in high surface area powders.

Influence of nitridation environment on the nitridation kinetics of a high surface area ( $\approx 63 \text{ m}^2/\text{g}$ ) attrition milled Type-B silicon powder was investigated at  $1250^\circ\text{C}$  and  $1350^\circ\text{C}$ . The results shown in Fig. 3 indicate nitridation environment had no significant influence on the nitridation kinetics of this powder. In contrast, addition

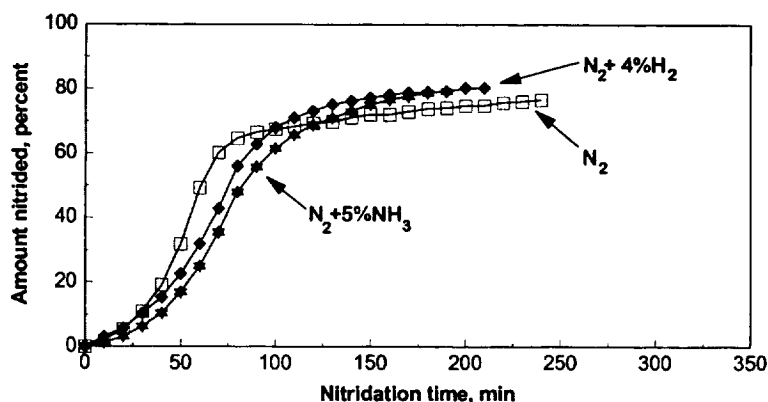


Fig. 3. Influence of nitridation environment on nitridation kinetics at  $1250^\circ\text{C}$  for 48hr attrition milled Type-B silicon powder compacts ( $\text{SA} \approx 63 \text{ m}^2/\text{g}$ ).



of small amounts (<5 vol%) of  $H_2$  or of  $NH_3$  to  $N_2$  is proven to enhance nitridation kinetics of low surface area commercially available silicon powders [8-9]. Phase analysis and oxygen ratio of the compacts after 4 hr nitridation in  $N_2$ ,  $N_2+4\%H_2$ , and  $N_2+5\%NH_3$  at  $1250^\circ C$  or at  $1350^\circ C$  are summarized in Table V. This table shows that at 1250 or at  $1350^\circ C$ ,  $H_2$  and  $NH_3$  additions to  $N_2$  promote formation of  $Si_2N_2O$  except for the compacts nitrided at  $1350^\circ C$  in  $N_2+4\%H_2$ . At a fixed nitridation temperature, the nitridation environment appears to have had no effect on the  $\alpha$ -/ $\beta$ - $Si_3N_4$  ratio except for compacts nitrided for 4 hr at  $1350^\circ C$  in  $N_2+5\%NH_3$ , but the ratio appears to decrease with increasing nitridation temperature. On the other hand, the oxygen ratio ranged from 0.66 to 0.93 and no discernible trend was noticed with nitridation environment or temperature.

Table V. Effects of nitriding environment and temperature on phase compositions and oxygen ratio of nitrided 48-hr-attrition-milled Type-B silicon powder compacts ( $SA \approx 63 \text{ m}^2/\text{g}$ ).

Nitriding conditions	$\alpha$ - $Si_3N_4$ , wt%	$\beta$ - $Si_3N_4$ , wt%	$\alpha/\beta$ ratio	Unreacted silicon, wt%	$Si_2N_2O$ , wt%	Oxygen ratio@
$N_2, 1250^\circ C, 4 \text{ hr}$	15.4	48.5	0.32	33.1	3.4	0.77
$N_2+4\%H_2$ , $1250^\circ C, 4 \text{ hr}$	15.5	58.0	0.27	19.7	6.8	0.83
$N_2+5\%NH_3$ , $1250^\circ C, 4 \text{ hr}$	14.7	57.5	0.26	20.7	7.1	0.93
$N_2, 1350^\circ C, 4 \text{ hr}$	9.1	73.5	0.12	10.7	6.8	0.66
$N_2+4\%H_2$ , $1350^\circ C, 4 \text{ hr}$	8.5	75.9	0.11	15.6	0	0.89
$N_2+5\%NH_3$ , $1350^\circ C, 4 \text{ hr}$	3.1	77.3	0.04	7.6	11.9	0.87

@ Ratio of oxygen after nitridation to oxygen before nitridation

### Effect of preoxidation on nitridation kinetics

To study the influence of oxidation on nitridation kinetics, the 48-hr-attrition-milled Type-B powder compacts ( $SA \approx 63 \text{ m}^2/\text{g}$ ) were first oxidized in air to 5 or 10 wt% gain to grow an additional layer of silica on the silicon. These compacts were then nitrided in  $N_2$  or in a  $N_2+4\%H_2$  mixture at 1250 for 4 hr; see

Fig. 4. For comparison purposes, the nitridation kinetics of the unoxidized silicon compacts are also included in the figure. Clearly, as the degree of preoxidation increases, the incubation period for the start of the nitridation reaction also increases and the nitridation rate decreases. The nitridation rate of the 5-percent oxidized compacts nitrided in  $N_2$  was generally lower in the initial stages, but after 4 hr, the percentage converted to  $Si_3N_4$  reached a level almost to that of the unoxidized powder. The 10-percent oxidized compacts, on the other hand, were only partially nitrided in  $N_2$ . In the  $N_2+4\%H_2$  environment, however both the 5- and 10-percent oxidized powder compacts were significantly nitrided, although the nitridation rate in the initial stages was slower.

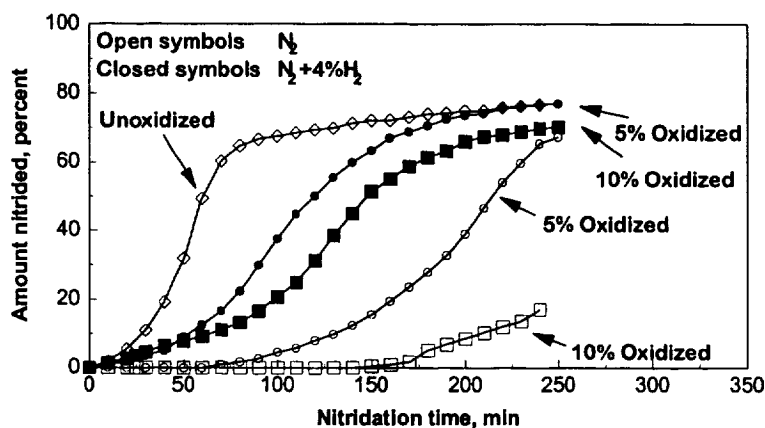


Fig. 4. Influence of nitridation environment on 48hr attrition milled and preoxidized silicon powder compacts ( $SA \approx 63 \text{ m}^2/\text{g}$ ) nitrided at  $1250^\circ \text{C}$ .

## SUMMARY OF RESULTS

The surface area of commercially available silicon powders was increased by wet attrition milling to facilitate processing and conversion to  $Si_3N_4$ . The influence of surface area, the nitridation environment, and preoxidation on the nitridation kinetics of the silicon powder compacts were investigated. Key findings are as follows:

- (1) With increasing attrition milling time, the surface area of silicon powder increases but impurities also accumulate in the powder due to wear of attrition mill components.
- (2) At a given temperature, as the surface area of the silicon powder increased, so did the percentage nitridation after 4 hr, but the  $\alpha/\beta$  ratio decreased. The silicon

powders having surface area  $> 40 \text{ m}^2/\text{g}$  can be nitrided to 70-percent conversion or greater in 4 hr at  $1250^\circ\text{C}$  or above.

- (3) Variation in % nitridation of the as-received silicon powder lots is due to transition metal impurities.
- (4) The nitridation environment had no significant influence on the nitridation kinetics of high-surface-area silicon powder compacts.
- (5) Preoxidation of high-surface-area silicon powder compacts retarded nitridation kinetics. However, the deleterious effects of oxidation could be overcome by nitriding the preoxidized compacts in an  $\text{N}_2/\text{H}_2$  mixture.

## CONCLUSIONS

The high-surface-area silicon powders can be prepared by attrition milling commercially available silicon powders. However during attrition milling wear of the grinding medium invariably introduces impurities into the silicon powder. By controlling the particle size of, and limiting impurities in the attrition milled silicon powder, a low temperature processing cycle required for RBSN composite fabrication can be developed. However, additional studies are needed to determine stability of SiC fibers under these processing conditions.

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